SCIENCE FOR GLASS PRODUCTION

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LOW SILICA $K_2O - Nb_2O_5 - SiO_2$ NONLINEAR OPTICAL GLASSES

V. N. Sigaev,[1,3] V. S. Ryzhenkov,[1] N. V. Golubev,[1] S. V. Lotarev,[1] and S. Yu. Stefanovich[2]

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Glasses with the compositions $(100 - x)KNbO_3 - xSiO_2$ (x = 12 – 35), forming a transparent glass ceramic when heat-treated in the glass formation temperature range, have been obtained. The initial stages of phase separation are accompanied by the appearance of appreciable quadratic optical nonlinearity in the glasses. This nonlinearity can be used to develop high-efficiency electro-optic modulators by thermal poling.

Key words: potassium niobate, nonlinear optics, second-harmonic generation, glass, glass ceramic.

Attempts to generate the second harmonic in glasses by thermal poling (polarization in a strong constant electric field at elevated temperatures) have been made repeatedly in the last two decades in order to develop a new generation of electro-optic modulators and frequency converters in which high quadratic optical susceptibility is combined with the complete absence of the piezoelectric effect. The latter is always present in nonlinear-optical crystals, and much more complex instrumentation is needed to suppress the effect. In addition, the index of refraction of the modulator material can be fully matched with that of the other components of the waveguide channel simply by varying the composition of the glass.

Up to now thermal poling has been applied predominately to phase-uniform glasses — quartz glasses doped with Ge, OH groups, and alkali cations [1] — and multicomponent glasses containing alkali cations and cations forming oxygen polyhedra with high polarizability (Ti, Nb, Te, Pb, and others) [2]. Thermal poling makes it possible to create in glass a highly effective nonlinear optical layer up to several microns thick, whose quadratic optical susceptibility $\chi^{(2)}$ reaches about 5 pm/V [3] in individual cases [3], i.e., it is comparable to that of lithium niobate and other nonlinear optical crystals. One possible promising direction for increasing the quadratic optical nonlinearity (QON) in glasses is to increase the niobium content and to nanostructure the glass by means of niobium-containing phases. According to [4], nanostructuring glass by means of crystals increases the QON substantially but data in [5] show that nanocrystallization has a negligible effect on $\chi^{(2)}$.

Hypotheses explaining the high QON of niobium-containing glasses subjected to thermal poling are usually based on the ideas of partial migration of singly charged cations in the interior volume of the glass from the anode to the cathode and the presence of distorted niobium polyhedra in the glass [6]. It is known that the high polarizability of the niobium-containing glasses is due to the high anisotropy of the NbO_5 and NbO_6 polyhedra, which is manifested in the enormous (up to 0.55 Å) variance of the Nb – O bond lengths [7]. Consequently, it can be supposed that as their fraction increases, the possibilities of poling in the formation of high QON increase. Glass formation in the systems $Me_2O - Nb_2O_5 - SiO_2$ (B_2O_3, P_2O_5, GeO_2) occurs with glass-former content of at least 20%,[4] but most studies of niobium-containing glasses have been performed for compositions with SiO_2 and B_2O_3 of 40% and higher [8, 9].

To increase the influence of poling on QON we believe that in addition to increasing the niobium content it is very important to produce QON in the initial glass by means of nanostructuring of the glass via the mechanism proposed in [10]. It is shown in the latter study that in alkali-niobium-silicate glasses containing of the order of 50% SiO_2 the QON is initiated during amorphous phase separation at temperatures near the glass formation temperature t_g.

[1] D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia.
[2] L. Ya. Karpov Institute for Scientific Research in Physical Chemistry, Moscow, Russia.
[3] E-mail: vlad.sigaev@gmail.com.

[4] Here and below — molar content.

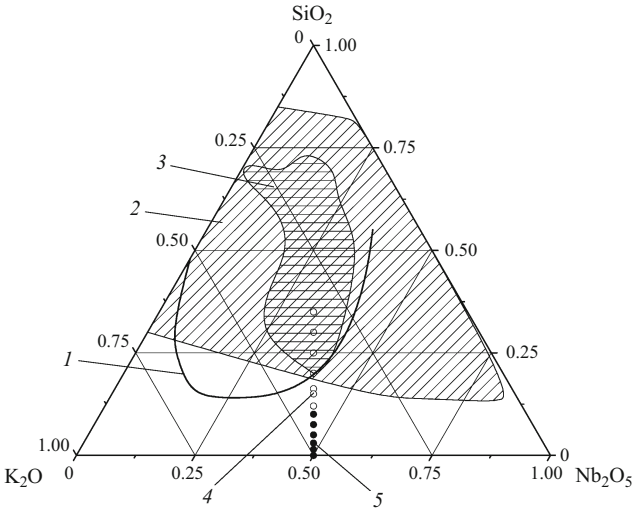

Fig. 1. Glass formation region in the system $K_2O - Nb_2O_5 - SiO_2$ for different cooling conditions: *1*) melt pressed on a metal plate [8] (founding in a quartz crucible); *2*) melt cooled in a platinum crucible in air [9]; *3*) compositions studied in [11]; ○, ●) glasses, studied in the present work, with compositions on the line $K_2O/Nb_2O_5 = 1$, which were obtained by pressing (*4*) and blowing the melt (*5*).

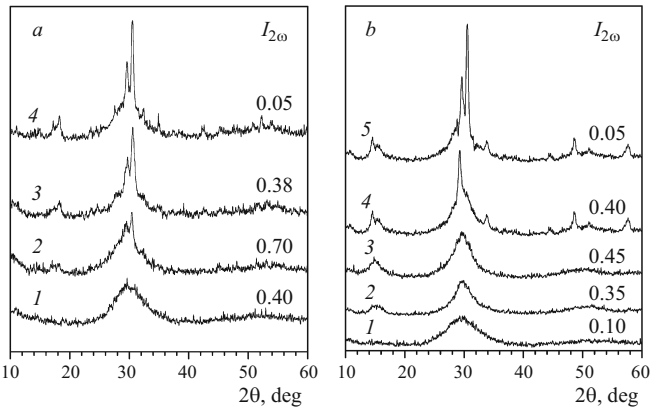

Fig. 2. X-ray diffraction patterns and the corresponding SHG signals ($I_{2\omega}$) of the glasses KNS-15 (*a*) and KNS-25 (*b*) without heat-treatment (*1*) and heat-treated at 590 and 610°C, respectively, for 24 (*2*), 36 (*3*), 48 (*4*), and 60 h (*5*).

It is quite likely that thin glass plates which are convenient for studying crystallization and optical and nonlinear optical properties as well as for thermal poling can also be obtained with a lower glass-former content by cooling the samples more quickly. However, almost nothing is known about the glass-formation and crystallization properties of glasses of this kind. Reducing the glass-former content to a minimum while at the same time maintaining technologically acceptable conditions for obtaining glass is very interesting for elucidating the mechanisms for the appearance of nonlinearity in glasses as well as for creating high-efficiency nonlinear optical glassy media by means of poling.

The present work is devoted to studying glass formation and crystallization of glasses in the system $K_2O - Nb_2O_5 - SiO_2$ (KNS) with $K_2O/Nb_2O_5 = 1$ and SiO_2 content less than 40% as well as to studying the nonlinear optical properties of low-silicate KNS glasses by the method of generating the second optical harmonic (SHG) as a function of the nanoscale structural changes at the initial stages of phase separation and crystallization. We attempted to obtain glasses with the compositions $(100 - x)KNbO_3 - xSiO_2$ (where x varies from 35 to 0), which we denote as KNS-x. The position of the experimental compositions in the ternary diagram is shown in Fig. 1 (circles).

The glasses with the compositions indicated above were made in a platinum crucible at temperatures 1250 – 1400°C depending of the SiO_2 content. Glass plates with thickness 0.5 – 1.5 mm were obtained by pressing melt with cooled metal plates. The amorphousness of the samples and their crystallization processes with subsequent heat treatments were studied by x-ray diffraction. All amorphous samples were investigated in the temperature range 20 – 1000°C by the DTA method with heating rate 10 K/min. The nonlinear optical properties of the glasses and their crystallization properties were tested by the SHG method using the procedure described in [12]. A Nd : YAG laser operating at 1064 nm in the Q-switching mode was used to perform the measurements. The intensity ratio $I_{2\omega}/I_{2\omega}$ (α-SiO_2) of the second harmonic radiation from the sample to the SHG signal from a standard α-quartz powder with particle size 3 – 5 μm was taken as the magnitude of the SHG signal. A JSM 7500 FA JEOL scanning electron microscope was used to perform the electron-microscopic investigations.

Glasses in the form of plates with no indications of crystallization were obtained for compositions with x ranging from 35 to 12. They were characterized completely by amorphous x-ray diffraction patterns (Fig. 2). For $x < 0.12$ partial crystallization of the glass was observed even during the formation process and intensified with decreasing silica content. Correspondingly, the microstructure of the initial pressed glasses was strongly nonuniform right up to the composition KNS-25.

Electron microscopy shows that phase inhomogeneities in the initial KNS glasses ranged from 10 to 20 nm in size. The inhomogeneity of the glasses intensified as the silica content decreased. Typical photomicrographs of KNS glasses are presented in Fig. 3. It is of interest that there is virtually no growth of the inhomogeneities in a quite wide temperature range. Thus, at 610°C, which is 60°C higher than the value of t_g for KNS-15 glass, after heat-treatment for 4 h the inhomogeneities grow only up to 20 – 30 nm but the interphase boundaries are much sharper. The XPA data attest that crystalline formations appear in the glass after prolonged heat-treatment — 36 h at 590°C and 48 h at 610°C for KNS-15 and KNS-25 glasses (see Fig. 2), respectively — and that after such heat-treatment the glass starts to opalesce and its light-transmission decreases sharply (the x-ray diffraction patterns *1* and *2* in Fig. 2*a* and *1 – 3* in Fig. 2*b* were obtained for transparent samples).

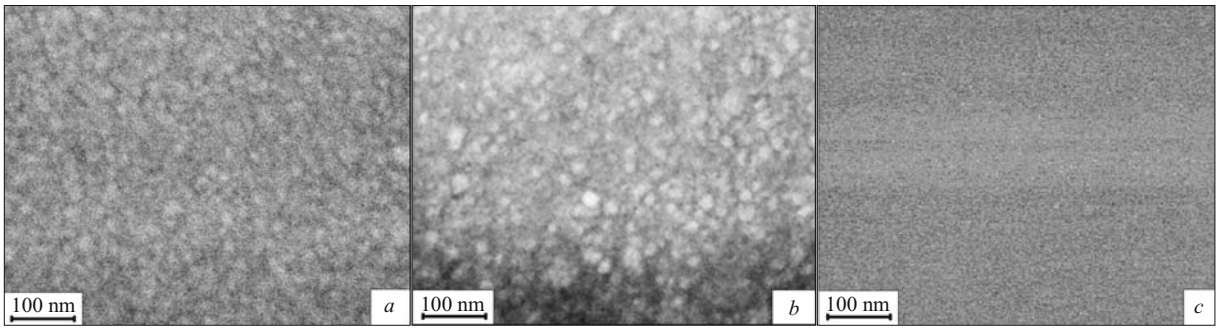

Fig. 3. Electron micrographs of the glasses: *a*) KNS-15 initial glass; *b*) KNS-15 glass heat-treated at 610°C for 4 h; *c*) KNS-25 initial glass.

It is possible that at temperatures close to t_g a process of chemical differentiation and ordering occurs with no appreciable particle growth while at the same time the transparency of the glass is preserved. Since this process can be used to control the heat-treatment regimes and to change the concentration gradient smoothly near interphase boundaries, following the approaches developed in [10], the observed nanosize inhomogeneities could be responsible for the appearance of QON in the glasses.

Indeed, testing of all initial and heat-treated glasses by means of SHG showed that they all exhibit QON which varies in a regular manner as a function of the composition and heat-treatment conditions. The curves of SHG versus the duration of heat-treatment of KNS-15 and KNS-25 glasses are displayed in Fig. 4. The SHG signal intensities are also presented on the x-ray diffraction patterns (see Fig. 2). They grow with increasing heat-treatment duration and temperature (i.e., in the course of chemical differentiation and ordering) right up to the appearance of opalescence, after which they descend rapidly with crystallization developing and loss of transparency. The absence of an SHG signal from the unidentified crystalline phase precipitating in KNS glasses (see Fig. 2) attests to its centro-symmetric structure.

In summary, low-silicate nanostructured glasses with quadratic nonlinearity whose thermal poling will make it possible, evidently, to increase the Pockels linear electro-optical effect substantially as compared with uniform polarized glasses which do not exhibit QON in the initial state, can be obtained in the KNS system in a wide range of compositions, temperatures, and heat-treatment times.

The KNS nonlinear optical glasses with low silica content are promising for developing high-efficiency linear electro-optical modulators for ultra-fast control of light fluxes in opto-electronics and in switching technologies.

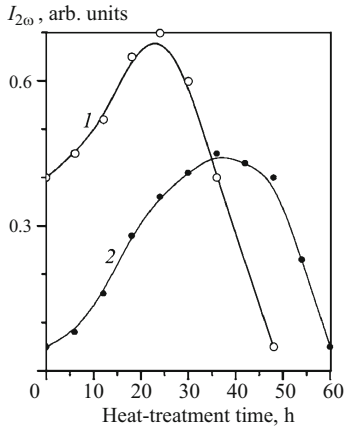

Fig. 4. SHG signal of glasses versus the heat-treatment time: *1*) KNS-15 composition, heat-treatment at 590°C; *2*) KNS-25 composition, heat-treatment at 650°C.

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